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A Monte Carlo Simulation Describing Melting Transition of Si–Type Structure in the Condensed Phase with BCC Lattice Model Including Many–Body Interactions*

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A new lattice model is proposed for Si crystallization from molten state, which is based on Monte Carlo (MC) simulation. In this model, each atom is allowed to move only on BCC lattice sites, and the potential energy of atom depends on the configuration in the 1st nearest neighbors. With the parameter that only the atoms constructing tetrahedron have lower energy than others, the 1st–order phase transition between diamond and random structures is observed, including a hysteresis behavior. On the other hand, with using a parameter set which is defined as a function of the number of the 1st nearest neighbors and the bond angles, which is determined by using genetic algorithm, the state is continuously changed with temperature.

KEYWORDS: lattice model, Monte Carlo simulation, genetic algorithm, 1st–order phase transition, crystal growth, silicon

1. Introduction

According to the industrial requirement, it is quite important to clarify theoretically local configurations of Si, which are thermodynamically stable or metastable, being realized during crystal growth, and melting processes in detail by numerical simulations. Several atomic–scale Molecular Dynamics (MD) [1] – [4] and Car–Parrinello method [5] have been performed on melt and crystalline Si. Strictly speaking, although the pair–correlation function has been compared with experiments [6], they are severely constrained both in time scale and in system size, and the crystal growth process has not yet been properly treated. In order to study thermodynamic equilibrium and discuss hysteresis behavior or metastable configurations for solidification and melting processes, a lattice Monte Carlo (MC) simulation is superior to those deterministic methods in many respects.

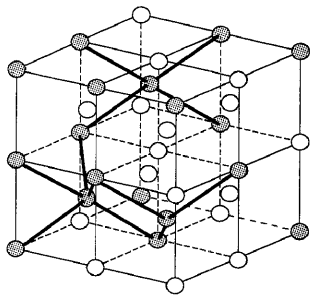
A new lattice model which explicitly takes many–body interactions into account was proposed by the present authors [7] to describe dynamically the crystal growth and melting processes. In the present paper, genetic algorithm is introduced to determine more efficiently the parameter set in the model. The nucleation process is simulated more quantitatively in the following.

2. Model

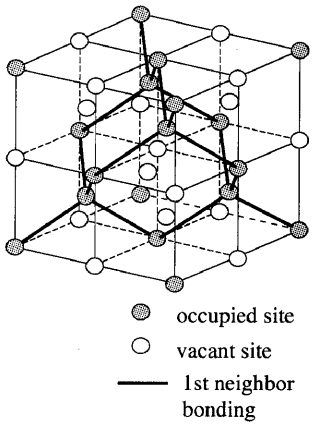
In this chapter, we describe the model which we use in the present study. First, we propose a BCC lattice model, which enables us to describe the behavior of melting process of Si in the condensed phase. Next, we mention to the two potential parameter sets which we assume in this study, one of which is defined by using genetic algorithm (GA). Finally, we mention GA.

2.1 BCC lattice model

The present lattice model is based on the assumption that each atom is allowed to move only on the BCC la-



(a) Liquid state (disorder phase).



(b) Solid state (diamond structure).

Figure 1. Schematic diagram of BCC lattice model with 50% filling.

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ttice sites. 50 % filling on the BCC lattice leads to the diamond structure for the ordered phase. As an example, 2×2×2 BCC cells are shown in Fig. 1. Figure 1(a) shows a sample of liquid state, where atoms occupy BCC sites in disorder. In contrast, Fig. 1(b) is the case where the atoms occupy these sites in order and the diamond structure is realized. In the present model, there are four different orientations for diamond structure. They are mutually identical either by shifting all the tetrahedrons consisting of 5 Si atoms centered at the body–center positions along the X–axis (or Y–axis) by one BCC cell, or by rotating the system around one of the Cartesian coordinates (X,Y, or Z) by 90°. Figures 2 (a)–(d) show the 4–equally stable diamond structures. In both cases the lattice occupation is set to be 50 %.

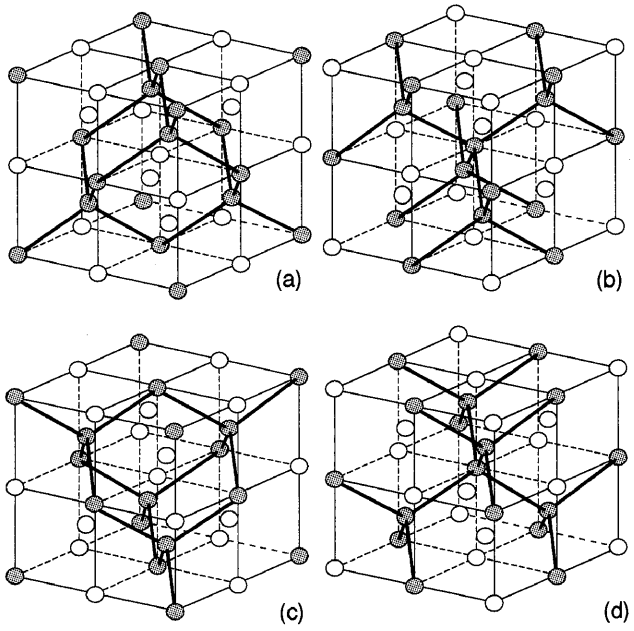


Figure 2. Schematic diagrams of the 4–equally stable diamond structures.

It is possible to define the liquid state not by measuring the pair–correlation function, but by the coordination number of Si, since the coordination number of Si is 4 in the solid state, while it is 6 or more in the liquid state for stable coordinations [8]. Here, the coordination number is defined by the sum of the numbers of the 1st and 2nd nearest neighbors.

Each atom moves one by one to the nearest neighbors using the Metropolis method [9]. The 3–dimensional periodic boundary condition is applied. We start from the liquid state, which is realized by keeping temperature slightly higher than the melting temperature for 2,000 MC steps. Then if the temperature is held constant (quenching or heating), the system becomes finally in the equilibrium. On the other hand, the same model is also applied to examine the melting of a single crystal. The size of the system in this study is 8×8×8 diamond lattice sites (4,096 atoms).

2.2 Energy parameter set

Generally, any potential energy function ϕ describing interactions among N particles can be decomposed into one–body (ϕ_1), two–body (ϕ_2), three–body (ϕ_3), $\cdots$, and N–body (ϕ_N) (r_i : position of i–th atom) contributions as follows :

$$\phi(r_1,\cdots,r_N) = \sum_i \phi_1(r_i) + \sum_{i<j} \phi_2(r_i,r_j) + \sum_{i<j<k} \phi_3(r_i,r_j,r_k) + \cdots + \phi_N(r_1,\cdots,r_N). \quad (1)$$

It is well-known that at least up to three–body interactions are necessary to stabilize the diamond structure for the description of Si solid state. It is easy to include many–body interactions effectively to this model. Since Si is a semiconductor in the solid state, it is reasonable to assume that the energy of each atom is defined by configurations surrounding the 1st nearest neighbors. In this paper, the following two potential models are studied.

Arbitrary units can be used in these two cases, since energy and temperature are related to each other just by the Boltzmann factor. Moreover, not the absolute value but the difference between the two states is important.

2.2.1 Tetrahedron model

At first, we assume that only the atoms which construct tetrahedral structure is lower in energy than the other atoms, although the parameter ignores any energy dependence on configurations in the liquid state. We call this assumption as *Tetrahedron model*. The potential energy E is given as follows :

$$E = \begin{cases} -a \ (a>0) & \text{(for tetrahedron)} \\ 0.0 & \text{(for other structures)} \end{cases}. \quad (2)$$

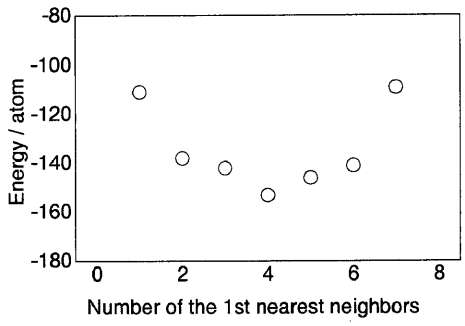
In this study, we simply set a = 10.0.

2.2.2 The number of the 1st nearest neighbors and the bond angle model

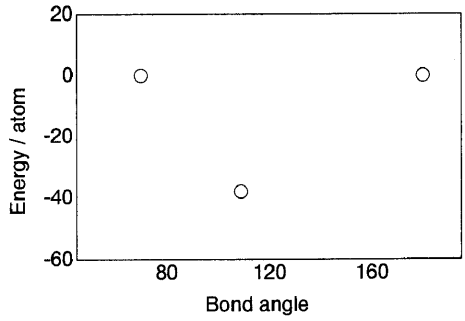
Next, the potential energy is assumed to be a function of the number of the 1st nearest neighbors($0 \sim 8$), and the bond angle between two nearest atoms (70°, 109° and 180°). We call this as *the number of the 1st nearest neighbors and the bond angle model.*

One of the most satisfactory potential parameter sets obtained so far by the genetic algorithm [10] [11] is shown in Fig. 3(a) and (b). (We mention the GA in the next section.)

Reduced temperature, which is independent of species, is applied to each model. Therefore it is possible to notice the tendency qualitatively of the melting process.



(a) Assumed relation between the number of the 1st nearest neighbors and the energy.



(b) Assumed relation between the bond angle and the energy.

Figure 3. Relations between the structure and the energy.

2.3 Genetic Algorithm

It is difficult to find directly the most satisfactory parameter set in the case where there exist many parameters, such as *the number of the 1st nearest neighbors and the bond angle model.* Because the number of candidates grows exponentially with the number of the parameters. It is well known that genetic algorithm (GA) is a useful technique to solve such kind of problems, and a similar study has already been performed [12]. Here, we present how to determine a satisfactory parameter set for arbitrary model potential.

Figure 4 is a brief flowchart of GA. Starting with a population of candidate parameter set, we simulate the evolution of the system and obtain satisfactory results. Then we select suitable parameter sets by using the following criterion. In this study, the criterion is evolution tendency to yield the diamond structure wide spread. A fraction of the population is selected as "parents". The next generation of candidate set is produced by hybridization of these parents. At the same time, it is needed to occur mutation to "hop" from one local minimum to another and permit an efficient sampling in the total phase space. The process is repeated many times, and finally one of the satisfactory parameter sets is realized. However, we must not forget that there is no guarantee for the obtained parameter set to be the best one.

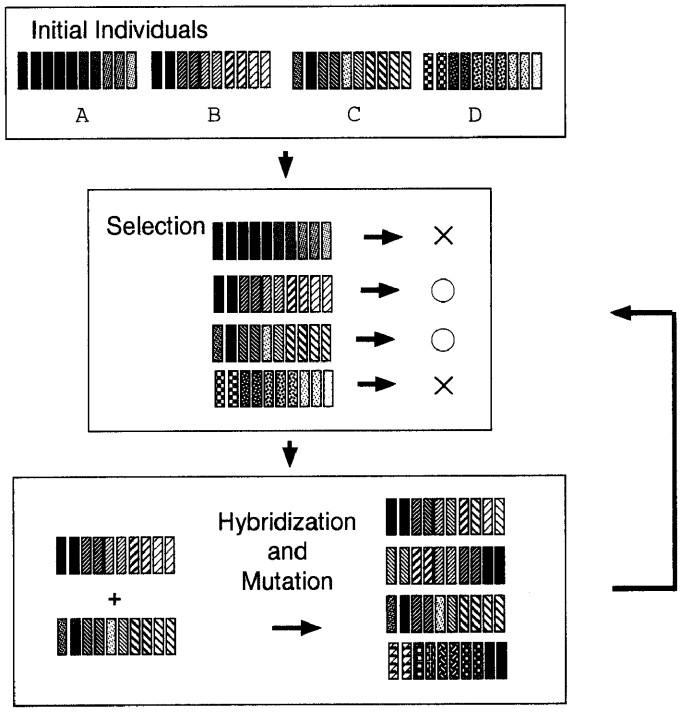


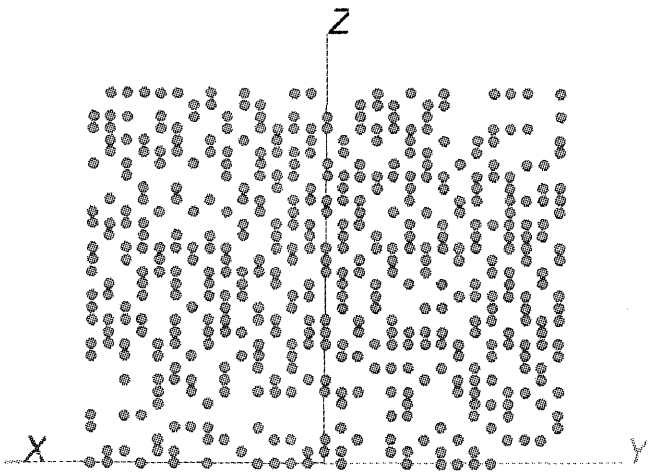
Figure 4. Flowchart of Genetic Algorithm. The algorithm includes the rotation of hybridization and mutation of these candidates to realize an efficient sampling of the phase space.

3. Results and Discussion

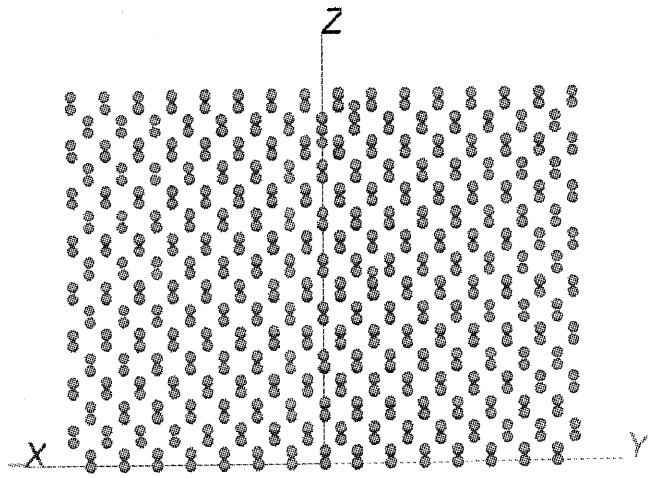
In low temperature region, both models yield the diamond structure at the thermal equilibrium, if the system is approached from the liquid state. The results obtained by the above two models are discussed in the following section.

3.1 Tetrahedron model

Figure 5(a) shows a sample of initial conditions in the present simulation. The system is shown as a view from the direction of $< 110 >$. This is a 50% filling random distribution of atoms on the BCC lattice. After 20,000 MC steps, we finally obtained a solid Si structure shown in Fig. 5(b), where the hexagonal pattern of the diamond structure is clearly achieved in the whole simulation cell.



(a) A sample of the initial distribution of the liquid state after equilibration from the random atomic positions.

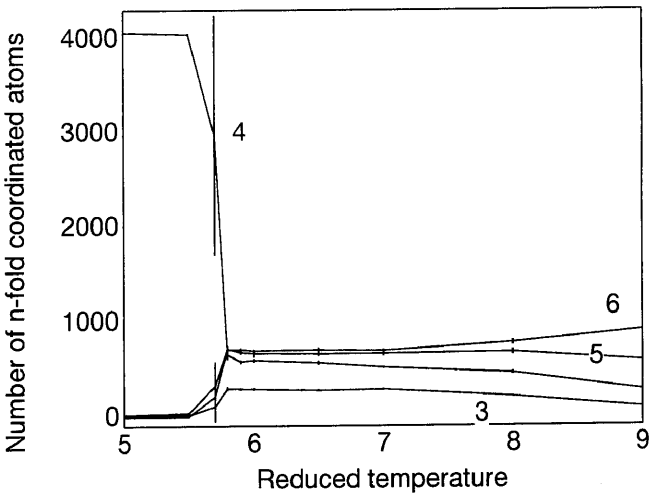


(b) A sample of the solid state structure obtained by quenching the liquid after 20,000 MC steps. There exist the hexagonal patterns of the diamond structure.

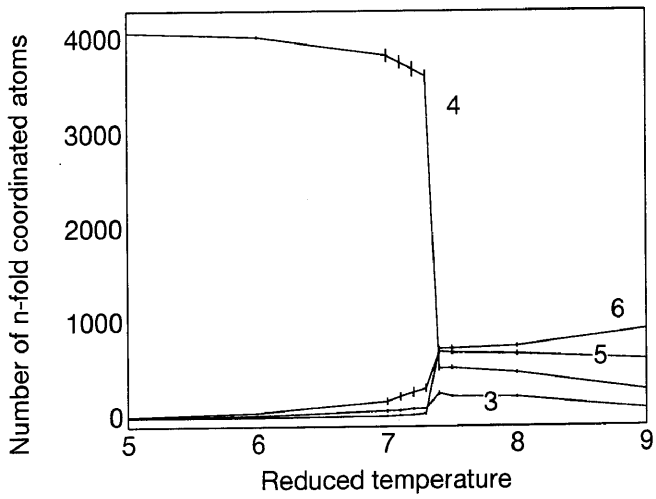
Figure 5. Samples of the results of the present simulation. (shown in the direction of $< 110 >$)

Figure 6 shows the final distributions of n–fold coordinated atoms as functions of temperature after 20,000 MC steps. Figure 6(a) is the result starting from the liquid state and (b) from the solid state, respectively. It is confirmed that the 4–fold coordinated atoms mainly exist in the low temperature region. Suddenly, at around 6 reduced temperature in Fig. 6(a) and around 7 in Fig. 6(b), higher coordinated atoms appear instead of the 4–fold one as temperature increases.

By comparing these two results (Fig. 6(a) and (b)), a hysteresis and a 1st–order phase transition is confirmed in this model, with a super cooling state.



(a) From liquid state.



(b) From solid state.

Figure 6 Final distribution of n-fold coordinated atom as a function of temperature after 20,000 MC steps.

Next, we discuss dynamics of cluster formation in the supercooling region. Figure 7 shows time evolution of the largest cluster size at several temperatures which are slightly lower than the melting point. This figure shows that stronger supercooling leads to faster nucleation. In other words, as temperature becomes high, there exists a long incubation period. Since there is no incubation period at the temperature region 5.0–5.5, it is considered that these states exhibit in the spinodal region.

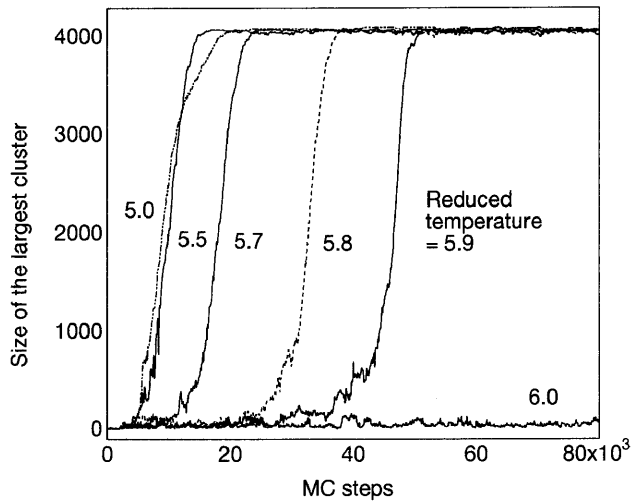


Figure 7. Relation between the largest cluster and MC steps with various temperatures which are slightly lower than the melting point.

3.2 The number of the 1st nearest neighbors and the bond angle model

Figure 8 illustrates the percentage of the atoms which construct diamond structure versus the number of genetic hybridization operations. Open circles are the result of the present GA simulation. The solid line, which is obtained by method of least square fitting for the good results of constructing diamond structure at least 70 %, indicates the tendency that the percentage of the diamond structure increases as the genetic operations. During the initial several generations, the percentage of the diamond structure quickly increases and all the obtained parameter sets consist of reasonable candidates. We find similar tendency for the satisfactory candidates which are obtained after a number of genetic operations (>10) that they have the most stable potential energy with the number of the 1st nearest neighbors of 4 and the bond angle of 109°. That is the reason why we selected one of the most satisfactory potential parameter set (Figure 3 shows them). All the results reported in the remainder of the paper are based on them. Since the mutation occurs in GA, there also exist many parameter sets which do not construct diamond structure in wide area.

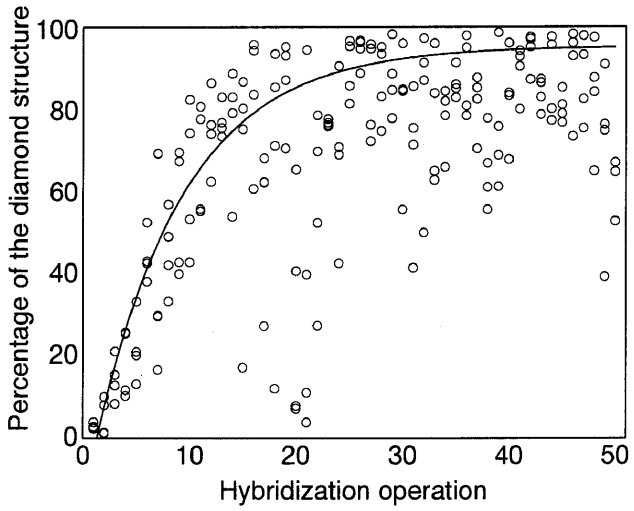
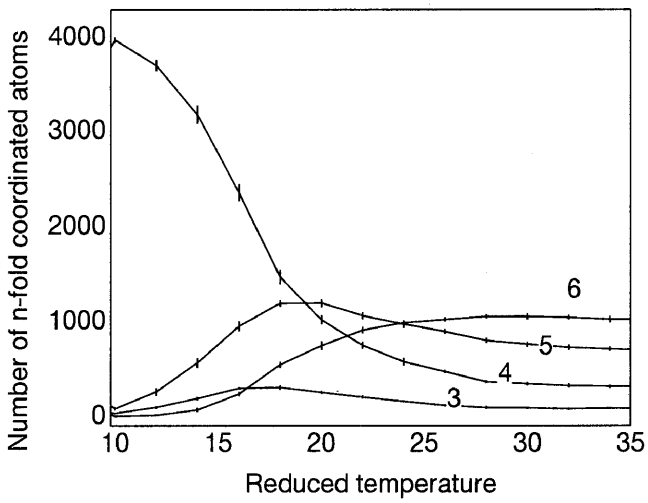
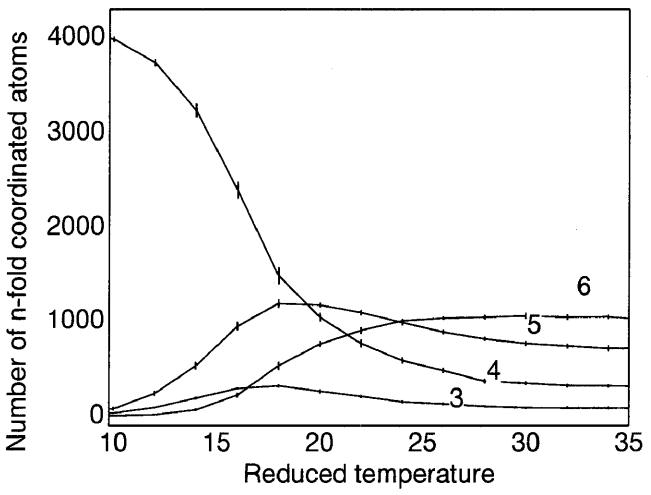


Figure 8. Percentage of the diamond structure versus hybridization operation. Open circles are the simulation results. The solid line, which is obtained by least squares fitting for the good results of constructing diamond structure at least 70 %, indicates the tendency that the percentage of the diamond structure increases as the genetic operations. The percentage of the diamond structure increases quickly in the initial stage, and the parameter set consists of reasonable candidates. Although, since the mutation occurs, there exist many parameter sets which do not construct diamond structure in wide area.

Figure 9 shows the final distributions of the n–fold coordinated atoms as functions of the reduced temperature after 5,000 MC steps. Figure 9(a) is the result starting



(a) From liquid state.



(b) From solid state.

Figure 9. Final distribution of n-fold coordinated atoms as functions of reduced temperature after 5,000 MC steps.

from the liquid state, and (b) from the solid state. However it is confirmed that the 4–fold coordinated atoms mainly exist in the low temperature region, and the numbers of higher coordinated atoms continuously increase with temperature. Furthermore, it is difficult to distinguish the two results, that is, there is no hysteresis behavior. This is because 5,000 MC steps, which is as the half of *Tetrahedron model*, is large enough to realize the thermal equilibrium for each temperature with this parameter model. It is important to consider that the behavior caused by the GA criterion does not show hysteresis behavior, but only to yield the diamond structure wide spread.

The present model is qualitatively successful to represent condensed phases in Si. We are planning to carry out much larger scale simulations to study nucleation process, solid–liquid interface and the bulk defects more accurately in the future.

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